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Production of dioxins and furans from the burning of excess gun propellant

*Isabelle Poulin
Sonia Thiboutot
Sylvie Brochu
DRDC Valcartier*

Defence R&D Canada – Valcartier

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Principal Author

Isabelle Poulin

Defence Scientist

Approved by

Pierre Lessard

Energetic Materials Section Head

Approved for release by

Christian Carrier

Chief Scientist

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Abstract

The burning of bags of excess gun propellant left over after an artillery exercise is a common practice on Canadian Forces Base (CFB) ranges and training areas. This process is carried out by aligning and burning the bags on the ground. This operation is known to leave significant quantities of energetic residues. It was also suspected of producing, among its combustion products, dioxins and furans, two structurally and chemically related chlorinated compounds known to be toxic and persistent in the environment. At CFB Petawawa, dioxins and furans were detected in some soil and water samples. The work reported here was aimed at studying the potential production of dioxins and furans from the combustion of gun propellants using a flare as an igniter. The results indicated that this production was not related to the combustion pattern, chemical composition or mass of the gun propellant, but to the presence of the igniter. The accepted procedure published by the Canadian Forces requires the use of a railroad fusee or a flare (like the warning flares used on roads at night) as the ignition source for the gun propellant. This trial should be replicated, and if further trials confirm that the railroad fusee is the source of the dioxins and furans, the disposal procedure for excess gun propellant by open burning should be modified.

Résumé

Le brûlage de gargousses excédentaires de poudre propulsive non utilisées après un exercice de tir de l'artillerie est pratique courante sur les champs de tir et d'entraînement des bases des Forces canadiennes (BFC). Ce procédé est effectué en alignant et en brûlant au sol les gargousses de poudre. Il est reconnu que cette opération laisse une quantité significative de résidus de matériaux énergétiques. Parmi les produits de combustion, cette procédure pourrait également produire des dioxines et des furannes, deux familles de produits chlorés structurellement et chimiquement semblables reconnus comme étant toxiques et persistants dans l'environnement. À la BFC Petawawa, des dioxines et des furannes ont été détectés dans certains échantillons de sols et d'eaux souterraines. Le travail présenté dans ce rapport visait à étudier la relation entre le brûlage de poudres propulsives et la production de dioxines et de furannes. Les résultats semblent indiquer que la production de ces composés n'est pas liée au modèle de combustion, à la composition chimique ni à la masse de poudre utilisée, mais à la présence de l'allumeur. La procédure prônée par les Forces canadiennes et publiée dans les documents internes exige l'utilisation d'une fusée éclairante (similaire à celles utilisées sur les routes pour la signalisation de nuit) pour l'allumage de la poudre. D'autres réplicats des tests devront être effectués et s'il est confirmé que la fusée est la source de la production de dioxines et de furannes, la procédure actuelle de disposition des gargousses non utilisées par brûlage devrait être modifiée.

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Executive summary

Production of dioxins and furans from the burning of excess gun propellant

Isabelle Poulin; Sonia Thiboutot; Sylvie Brochu; DRDC Valcartier TR 2009-365; Defence R&D Canada – Valcartier; January 2011.

Introduction or background: Conventional large-calibre ammunition for artillery (105- and 155-mm howitzers, for example) is composed of a projectile and separate charges of gun propellant. The propellant is contained in bags, and the number of bags is chosen depending on the distance to the target and the firing angle. Some bags are almost always removed before firing, and the excess bags have to be destroyed before the battery team leaves the training range. This destruction is carried out by aligning and burning the excess bags on the ground, using a railroad fusee for ignition. This operation is known to leave significant quantities of propellant and propellant residues on the ground. It was also suspected of producing, among its combustion products, dioxins and furans, two structurally and chemically related compounds known to be toxic and persistent in the environment. At some Canadian Forces Bases (CFBs), such as CFB Petawawa, soil and groundwater samples were contaminated with dioxins and furans. In the case of CFB Petawawa, their sources remain unidentified. The work reported here was aimed at studying the relationship between the open burning of excess bags of propellants and the production of dioxins and furans.

Results: The tests that were carried out indicated that the production of dioxins and furans was not related to the combustion pattern, mass or composition of the propellant, but to the presence of the igniter. The accepted procedure published by the Canadian Forces requires the use of a railroad fusee (like the warning flares used on roads at night) to ignite the gun propellant, and this leads to the production of undesired contaminants.

Significance: Incomplete combustion of organic material in the presence of a chlorine source is known to produce dioxins and furans. In the case of the combustion of excess gun propellant, the chlorine source is perchlorate from the railroad fusee. The accumulation of these compounds in the environment should be avoided.

Future plans: Other tests should be performed to confirm that the railroad fusee used as an ignition source is the source of the dioxin and furan production. If so, the procedure accepted by the Canadian Forces for the disposal of excess gun propellant by open burning should be modified. Ignition mechanisms that will not produce any undesirable reaction by-products should be studied and introduced.

Sommaire

Production of dioxins and furans from the burning of excess gun propellant

Isabelle Poulin; Sonia Thiboutot; Sylvie Brochu; DRDC Valcartier TR 2009-365; R & D pour la défense Canada – Valcartier; janvier 2011.

Introduction ou contexte: Les munitions conventionnelles d'artillerie de gros calibre, telles que celles utilisées par les obusiers de 105 et 155 mm, sont composées d'un projectile et d'une cartouche séparée remplie de poudre à canon. Cette poudre est contenue dans des gargousses de tissus et leur quantité est choisie selon la distance à la cible et l'angle de tir afin d'ajuster la trajectoire du projectile. Des gargousses sont généralement retirées de la cartouche avant la mise à feu et l'excès doit être détruit avant que le groupe de batterie ne quitte le site d'entraînement. Cette destruction est réalisée en alignant les gargousses excédentaires au sol et en les brûlant en utilisant une fusée éclairante comme source d'allumage. Il est reconnu que cette opération laisse des quantités significatives de poudre propulsive et de résidus de poudres au sol. On la soupçonne aussi de produire, parmi ses produits de combustion, des dioxines et des furannes, deux familles de composés chlorés structurellement et chimiquement semblables reconnus comme étant toxiques et persistants dans l'environnement. Sur certaines bases des Forces canadiennes (BFC), telles que la BFC Petawawa, certains échantillons de sols et d'eaux souterraines sont contaminés par des dioxines et des furannes et leur source est toujours non identifiée. Le travail présenté dans ce rapport vise à étudier la relation entre la destruction de gargousses excédentaires par brûlage au sol et la production de dioxines et de furannes.

Résultats: Les tests réalisés semblent indiquer que la production de dioxines et de furannes n'est pas liée au modèle de combustion, ni à la composition chimique, ni à la masse de poudre à canon, mais bien à la présence de l'allumeur. La procédure publiée par les Forces canadiennes demande l'utilisation d'une fusée éclairante (similaire à celle utilisée pour la signalisation de nuit) pour l'allumage de la poudre à canon, ce qui entraîne la production de contaminants indésirables.

Importance: La combustion incomplète de la matière organique en présence d'une source de chlore est reconnue comme produisant des dioxines et des furannes. Dans le cas du brûlage de poudre à canon excédentaire, la source de chlore est le perchlorate contenu dans la fusée. L'accumulation de ces composés dans l'environnement devrait être évitée.

Perspectives: D'autres tests devaient être effectués pour confirmer que l'utilisation d'une fusée éclairante comme source d'allumage est la source de la production des dioxines et des furannes. Si tel est le cas, la procédure acceptée par les Forces canadiennes pour la destruction des gargousses excédentaires par brûlage devrait être revue et modifiée. Des

systèmes d'allumage ne conduisant à aucun produit de réaction indésirable devraient être étudiés et mis en place.

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Table of contents

Abstract	i
Résumé	i
Executive summary	iii
Sommaire	iv
Table of contents	vii
List of figures	viii
List of tables	ix
Acknowledgements	x
1 Introduction.....	1
2 Dioxins and furans.....	3
2.1 Regulations for dioxins and furans and calculation of the toxic equivalent quantity....	4
2.2 Dioxins and furans in residues from the burning of excess gun propellant: preliminary studies	5
3 Experiment.....	7
3.1 Gun propellant.....	7
3.2 Experiment set-up: gun propellant burning trial on surface soil	11
3.2.1 Gun propellant line configurations.....	11
3.2.2 Ignition method.....	15
3.3 Experiment set-up: the flare trial	18
3.3.1 Set-up description for burning on sand	18
3.3.2 Set-up description for burning on stainless-steel plates	20
3.4 Sampling.....	22
3.4.1 Sampling in the propellant burning trial on soil.....	22
3.4.2 Sampling for the flare trial: sand and stainless-steel table	24
3.5 Analytical method for determining dioxins and furans in solid samples	25
4 Results and discussion	26
4.1 Dioxins and furans in residues after the gun propellant burning trial on soil.....	26
4.2 Dioxins and furans in residues after the flare trial: sand and stainless-steel table.....	28
5 Alternate methods that reduce the production of dioxins and furans	31
6 Conclusion	32
References	33
Annex A .. Toxic equivalency factors.....	37
List of symbols/abbreviations/acronyms/initialisms	39

List of figures

Figure 1: General structure of PCDDs (n and m range from 0 to 4)	3
Figure 2: General structure of PCDFs (x and y range from 0 to 4)	3
Figure 3: Propellant bags (M67, 105-mm calibre)	8
Figure 4: Gun propellant bags (M3A1, 155-mm calibre).....	10
Figure 5: Schematic of a complete M3A1 propelling charge (155-mm calibre) [12]	10
Figure 6: 2,500-m firing corridor, METC Valcartier	11
Figure 7: Line set-up for burning gun propellant on the ground	12
Figure 8: Set-up for single-bag lines: a) line 105a (105-mm calibre); b) line 155a (155-mm calibre).....	13
Figure 9: Set-up for double-bag lines: a) line 105b (105-mm calibre); b) line 155b (155-mm calibre).....	13
Figure 10: Set-up for triple-bag lines: a) line 105c (105-mm calibre); b) line 155c (155-mm calibre).....	14
Figure 11: Typical flare, with a safety fuse for igniting the gun propellant: a) photograph of the set-up, b) schematic showing how a railroad fusee is prepared for ignition	16
Figure 12: Lines of propellant bags before ignition	17
Figure 13: Burning the gun propellant lines.....	17
Figure 14: Schematic of the set-up for the flare trial.....	18
Figure 15: Set-up for the flare trial: a) before and b) after combustion (lines 1 and 2).....	19
Figure 16: Set-up for the flare trial (the part with the flare only: line 3).....	20
Figure 17: Schematic of the stainless-steel burning table	21
Figure 18: The flare in one corner of the table	21
Figure 19: Gun propellant bags on the table before ignition.....	22
Figure 20: Set-up area: a) before the set-up installation (flags indicate the positions of the future gun propellant lines) and b) after the burning.....	23
Figure 21: Close-up of a line after combustion	24
Figure 22: Table after burning and sampling positions	25

List of tables

Table 1: Sources of dioxins in the environment [8]	4
Table 2: Results of the preliminary tests for dioxins and furans in solid residues from the open burning of excess gun propellant on snow	6
Table 3: Chemical composition of M1 gun propellant.....	7
Table 4. Masses of gun propellant in the charges of an M67 propelling charge (Weight Zone 2) [11].....	8
Table 5. Masses of M1 gun propellant in the charges of an M3A1 propelling charge (green bags) [12]	9
Table 6: Description of each line.....	14
Table 7: Numbers of bags of each increment in the 105-mm-calibre lines.....	15
Table 8: Number of bags of each increment in the 155-mm-calibre lines	15
Table 9: Concentrations of dioxins and furans, reported in toxic equivalent quantities, in the samples of gun propellant burned on soil.....	27
Table 10: Concentration of dioxins and furans, reported in toxic equivalent quantities, in the samples from the flare trial on sand	29
Table 11: Concentrations of dioxins and furans, reported in toxic equivalent quantities, in the samples from the flare trial on the stainless-steel table.....	30
Table 12: Toxicity equivalency factors (TEFs) for polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs), as proposed by the World Health Organization (WHO) [19]	37

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1 Introduction

Training with weapons, including live-fire training, is an important part of military activities. It ensures that troops are always in a high degree of preparedness for any potential mission. Among the weapons used, large-calibre howitzers, such as 105-mm and 155-mm howitzers, are common. At the end of most military exercises involving large-calibre weapon systems, unused bags of gun propellant remain. This is because the propelling charges of much large-calibre ammunition are composed of increments, and the number of increments is chosen to suit the target distance. The current practice is to dispose of excess propellant increments by open burning. This is done by positioning the charges on the surface of the ground, in a shallow trench, on a concrete slab or in metal trays and igniting them from a safe distance by means of an ignition train of combustible material [1].

Although this procedure is well established, its impacts on the environment are not fully understood. Burning, whether on snow cover, the ground or a combustion plate (concrete or steel), does not lead to complete combustion. Few studies on the characterization of these residues have been reported in the literature.

In the work of Walsh *et al.* [2-3], several expedient burn sites for mortar gun propellant in the field were studied to determine the deposition of gun propellant residues as a result of these disposal activities. Both residues containing energetics and "kicked-out" raw propellant grains have been found at burn and test sites, mostly on wet and snow-covered ground. The quantities were significant, being greater than 1% of the original nitroglycerine load in the case of mortar propellants. It was stressed that energetics from field-expedient disposal burns on the ground at firing points will be problematic for range sustainment. In Diaz *et al.* [4], gun propellant bags from 105-mm howitzers (M1 single-base composition) and 155-mm howitzers (white bags, M1 single-base composition) were burned in various configurations, and it was found that burning on snow cover led to the dispersion of 0.08% by total weight of unburnt 2,4-dinitrotoluene (2,4-DNT) (or 0.8% of the original 2,4-DNT load). This value is thought to be an underestimation, since the entire plume was not collected. Other contaminants, such as lead, can be spread by the burning of excess gun propellant. The complete list of combustion by-products remaining on the soil surface is not known at this moment.

Of the contaminants found at various ranges, dioxins and furans are among the most problematic. These families of compounds are highly toxic and very difficult to trace back to their sources. For example, at Canadian Force Base (CFB) Petawawa [5], dioxins and furans were detected in a scrap pit, and the source was clearly anthropogenic, without being easily identifiable.

The Old Grenade Range at CFB Petawawa also contained dioxins and furans at concentrations above the regulations in soil samples. For example, 6.1 ng TEQ/kg

(between 0 and 10 cm) and 5.3 ng TEQ/kg (between 10 and 20 cm) were measured in profile samples. They were also found in water outside the range and upgradient from it. The source remains unknown, but it was not linked to Agent Orange, a chemical used at this location [6].

Since it is well known that the combustion of many compounds produces dioxins and furans, one of the hypotheses raised to explain the presence of these compounds in Petawawa is that they were perhaps produced during the burning of excess gun propellant.

This report presents trials conducted in September 2008 and February 2009 to test the hypothesis that dioxins and furans are produced during the combustion of excess propellants. This work was sponsored by the Director of Land Environment (DLE), Department of National Defence, Canada, and by the US Strategic Environmental Research and Development Programme (SERDP) through project ER-1481.

2 Dioxins and furans

Polychlorodibenz-p-dioxins (PCDDs or dioxins) and polychlorodibenzofuranes (PCDF or furans) are two groups of planar aromatic chlorinated compounds with similar physico-chemical properties. The basic chemical structure of dioxins is shown in Figure 1 and of furans in Figure 2. There are 210 different congeners of dioxins and furans. They vary slightly in toxicity, but exposure to them has been linked to a wide range of adverse health effects in laboratory animals and humans, including chloracne and other skin disorders and lesions, liver problems, stomach cancer, impairment of the immune system, the endocrine system and reproductive functions, effects on the developing nervous system, other developmental events and certain types of cancers [7, 8]. Many of the effects are mediated through interaction with the aryl hydrocarbon receptor [8].

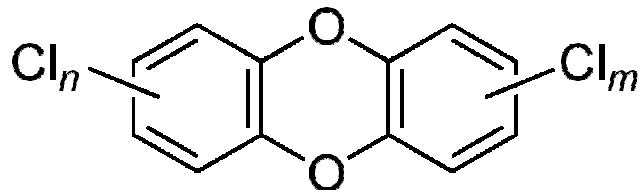


Figure 1: General structure of PCDDs (n and m range from 0 to 4)

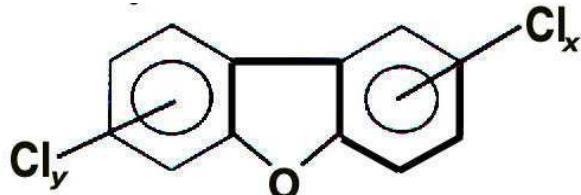


Figure 2: General structure of PCDFs (x and y range from 0 to 4)

Dioxins and furans are produced mainly by human activities. Multiple sources exist, and long-range transport can occur. The major identified sources of dioxins have been grouped into four categories, as shown in Table 1. They are persistent and bioaccumulate in the environment. Scientists have shown that they are highly resistant to biodegradation due to their very low solubility in water and high octanol-water partition coefficients [8].

Table 1: Sources of dioxins in the environment [8]

Source	Examples
Incineration	Municipal waste Hospital waste Hazardous waste Sewage sludge
Combustion	Cement kilns Wood burning Diesel vehicles Coal-fired utilities Crematorium facilities
Industrial processes	Pulp and paper mills Chemical manufacturing Metal industry
Other	Biochemical processes Photolytic processes Forest fires Accidental releases

2.1 Regulations for dioxins and furans and calculation of the toxic equivalent quantity

The concentrations of dioxins and furans in the soil and water and their daily intake by humans are regulated. Because they are rarely encountered individually in the environment, but are present in varying mixtures, the way to compare the toxicity of samples is to use a toxic equivalent quantity (TEQ). The congeners are standardized to a toxicologically equivalent amount of 2,3,7,8-TCDD, the most toxic congener. In other words, the most toxic congener, TCDD, is rated 1.0, and the less toxic congeners are rated as fractions [8]. The TEQ is calculated using Equation 1.

$$\text{Total TEQ} = \sum_{i=1}^n (C_i \times TEF_i) \quad (1)$$

Where:

TEQ: the toxic equivalent quantity, is the concentration of the mixture of congeners, expressed as an equivalent quantity of 2,3,7,8-TCDD

n: is the number of congeners (for which toxic equivalency factors (TEFs) are available)

C_i : is the concentration of congener i

TEF_i : is the toxic equivalency factor for congener i (can be found in Annex A)

The use of toxic equivalency factors (TEFs) assumes that the toxic effects are additive and act via a common mechanism to cause toxicity [8].

In Canada, the Canadian Council of Ministers of the Environment (CCME) [9] has stated that the recommendation for all land uses (agricultural, residential, commercial and industrial) is 4 ng TEQ/kg (4 pg TEQ/g). For drinking water, Health Canada has not issued a regulation for this parameter, but the province of Quebec, through the Ministry of Sustainable Development, Environment and Parks, has published a criterion of 15 pg TEQ/L (0.015 ng TEQ/L) for groundwater used for drinking [10]. In the US, the Environmental Protection Agency (EPA) has stated that the national regulation for drinking water is 0.03 ng TEQ/L [10].

2.2 Dioxins and furans in residues from the burning of excess gun propellant: preliminary studies

As stated in the introduction, Diaz *et al.* [4] conducted a trial in the winter of 2005 to study the accumulation of residual dinitrotoluenes from the open burning of gun propellant (155-mm calibre, M4 series, white bags) on pristine snow cover. Because the residues collected during this trial were kept in a freezer after Diaz's work, it was decided to analyse five samples from various burning scenarios to look for dioxins and furans. As the complete description of the trial can be found in Reference [4], it will not be repeated here in its entirety. As a brief summary, each burn was carried out separately on fresh snow cover, each with its own railroad fusee for ignition. A portion of the residues (roughly 80% of the plume in most trials) was collected with some of the snow into bags. The snow was melted and the residue recovered. The total mass of the residues was quite high, so only a small aliquot (10 g) was sent to a private company (Bodycote, Pointe-Claire, QC, Canada), which subcontracted to another laboratory (Pacific Rim Laboratories Inc., Surrey, BC, Canada) to analyse for dioxins and furans. The masses of

the gun propellant burned and the residues collected, as well as the results of the dioxin and furan analyses, are given in Table 2.

Table 2: Results of the preliminary tests for dioxins and furans in solid residues from the open burning of excess gun propellant on snow

Sample	Mass of gun propellant (kg)	Mass of residue collected (kg)	Concentration of PCDD-PCDF (pg TEQ/g)
1	73.176	1.648	ND
2	18.294	0.162	ND
3	18.294	0.130	29.5
4	36.588	0.652	31.8
5	1.261	0.057	10.9

ND: not detected

For three of the five samples, the TEQ was significantly higher than the regulation: 29.5, 31.8 and 10.9 pg TEQ/g, compared with the criterion of 4 pg TEQ/g. These results led DRDC scientists to believe that dioxins and furans may be produced by the open burning of excess gun propellant, but that the matter should be investigated in greater detail. The tests that were performed are described in Chapter 3, and the results are presented in Chapter 4.

3 Experiment

This section will describe the materials and set-ups used in the two trials that were conducted. The sampling and analysis for dioxins and furans will also be described.

3.1 Gun propellant

Gun propellants for howitzers of two different calibres, 105 and 155 mm, were used. The M67 propelling charge for the 105-mm howitzer [11] consists of a total of seven bags of gun propellant, weighing approximately 1.28 kg in total, filled with grains of M1 single-base composition. The chemical constituents of this gun propellant are shown in Table 3. The gun propellant for each charge increment is contained in a bag made of polyester-viscose rayon cloth, which is marked with the increment (charge) number and the lot number of the propellant inside. The #1 and #2 charges have 0.38-mm (FNH.015-inch) single-perforation type-II propellant for quick burning. The #3 to #7 charges have 0.71-mm (FNH.025-inch) multi-perforated (7-hole) type-I propellant for slower burning. Figure 3 is a photograph of #6 and #7 bags. For the trial, only #5, #6 and #7 charge bags were used, these being the bags burned most often in the field. The mass of the gun propellant in each bag is shown in Table 4.

Table 3: Chemical composition of M1 gun propellant

Constituents	Proportions (weight/weight %)
Nitrocellulose	85 ± 2
2,4-dinitrotoluene	10 ± 2
Dibutylphthalate	5 ± 1
Diphenylamine (added)	0.9 ± 1.2
Potassium sulphate (added)	1 ± 0.3



Figure 3: Propellant bags (M67, 105-mm calibre)

Table 4. Masses of gun propellant in the charges of an M67 propelling charge (Weight Zone 2) [11]

Charge #	Mass of gun propellant (kg)
1	0.245
2	0.040
3	0.072
4	0.110
5	0.114
6	0.260
7	0.406

Gun propellant bags for the 155-mm howitzer, i.e., M3A1 green-bag propelling charges [12], were also burned during the trials that were carried out. A full charge consists of

approximately 2.5 kg of single-perforated (0.381-mm/0.015-inch) cylindrical gun propellant of M1 composition. The propellant is contained in bolt-shaped cartridge cloth bags, dyed green, and is divided into a base charge and four increment charges. The mass of the propellant in each bag is given in Table 5, while the chemical composition is shown in Table 3. An igniter charge consisting of 99 g of clean-burning igniter (CBI) powder in a red cloth bag is sewn to the rear of the base charge (the #1 charge). The composition of CBI is a minimum of 98% nitrocellulose, 1.5% \pm 1.0 of diphenylamine, up to 0.1% of potassium nitrate and 0.2% of added graphite glaze. A flash reducer pad containing 57 g of potassium nitrate is assembled forward of the base charge. Similar 28.4-gram pads are assembled forward of the #4 and #5 increments. A photograph of #4 and #5 charge bags and a flash reducer pad of potassium nitrate appears in Figure 4. A schematic of a complete M3A1 propelling charge is shown in Figure 5.

Table 5. Masses of M1 gun propellant in the charges of an M3A1 propelling charge (green bags) [12]

Charge #	Mass of gun propellant (kg)
1	0.864
2	0.227
3	0.298
4	0.425
5	0.709



Figure 4: Gun propellant bags (M3A1, 155-mm calibre)

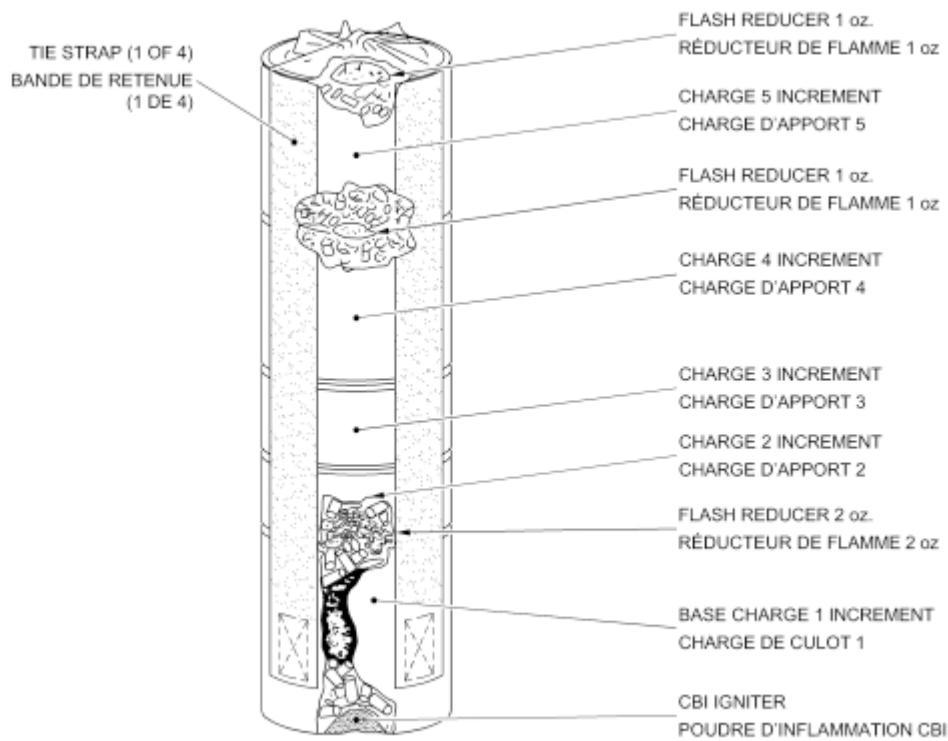


Figure 5: Schematic of a complete M3A1 propelling charge (155-mm calibre) [12]

All the gun propellant bags for both 105- and 155-mm calibres were obtained from the Canadian Forces via the Munitions Experimental Test Centre (METC). They were accumulated from various live-firing exercises held at CFB Valcartier. Instead of being burned after the exercises, the excess gun propellant bags were stored in plastic bags, which were placed inside thick triwall cardboard boxes, brought back to the METC and kept in storage.

3.2 Experiment set-up: gun propellant burning trial on surface soil

The first trial involved burning excess gun propellant bags directly on surface soil. It was held at the 2500-m firing corridor in the METC area located within CFB Valcartier on 23 September 2008. The GPS position of the set-up site was 0307269 – 5198999 (7-metre precision). This position was chosen because this site was probably not contaminated with dioxins and furans, since live-fire tests were almost the only activity at this site. The nearby presence of a sampling well for ground water was considered a potential asset. If a significant quantity of dioxins and furans were created during the trial, this well could be monitored for a period to check for leaching. The set-up was situated upstream from the well, as shown in Figure 6.



Figure 6: 2,500-m firing corridor, METC Valcartier

3.2.1 Gun propellant line configurations

The experiment set-up included a total of six lines of gun propellant bags. They were arranged for burning in three different configurations for each of the 105- and 155-mm calibres. The set-up is shown in Figure 7. The nomenclature included the calibre and a

letter indicating the type of line. The first line for each calibre was designated “a” (“105a” and “155a” for the 105- and 155-mm calibres, respectively). The “a” lines were composed of a single line of bags. Close-ups are shown in Figure 8. The bags were slightly overlapped to make sure the fire would travel the entire length of the line. The second line for each calibre was designated “b”. It was a double-bag line, as shown in Figure 9. Bags were placed two abreast and slightly overlapping lengthwise to ensure flame propagation. The last line for each calibre was designated “c”, and it was a triple-bag line, with two bags placed on the ground and a third placed atop the first two (in the middle), as shown in Figure 10. Descriptions of the lines are given in Table 6. The number of bags of each increment is shown in Table 7 for the 105-mm-calibre lines and in Table 8 for the 155-mm-calibre lines.

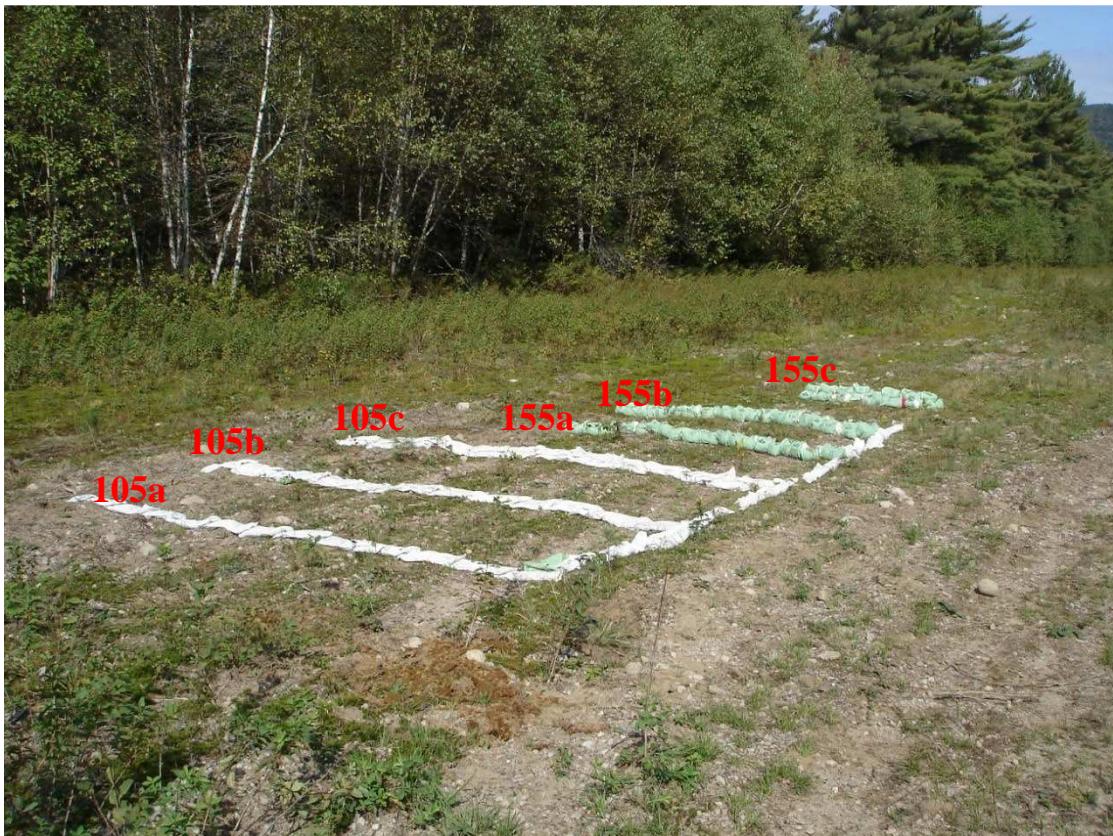
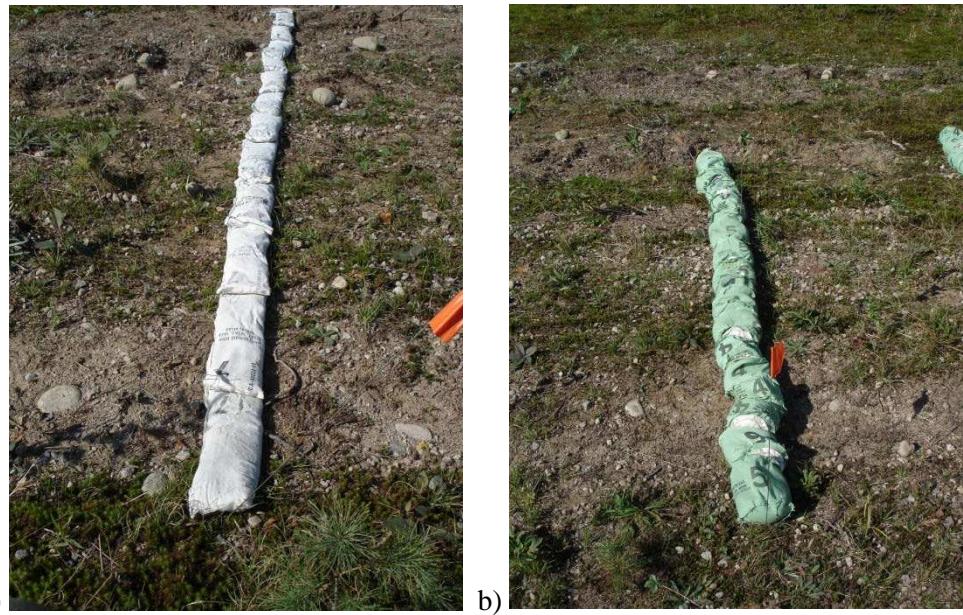


Figure 7: Line set-up for burning gun propellant on the ground



*Figure 8: Set-up for single-bag lines: a) line 105a (105-mm calibre);
b) line 155a (155-mm calibre)*



*Figure 9: Set-up for double-bag lines: a) line 105b (105-mm calibre);
b) line 155b (155-mm calibre)*



Figure 10: Set-up for triple-bag lines: a) line 105c (105-mm calibre); b) line 155c (155-mm calibre)

Table 6: Description of each line

Line	Type	Length (cm)	Width (cm)	Total mass of gun propellant (kg)
105a	Single-bag	304	10	5.278
105b	Double-bag	306	17	9.908
105c	Triple-bag	319	19	14.812
155a	Single-bag	209	14	10.49
155b	Double-bag	214	26	20.412
155c	Triple-bag	130	22	16.556

Table 7: Numbers of bags of each increment in the 105-mm-calibre lines

Line	Number of propellant bags		
	#5 charge (0.114 kg/bag)	#6 charge (0.260 kg/bag)	#7 charge (0.406 kg/bag)
105a	0	0	13
105b	0	10	18
105c	1	5	33

Table 8: Number of bags of each increment in the 155-mm-calibre lines

Line	Number of propellant bags				
	#1 charge (0.864 kg/bag)	#2 charge (0.227 kg/bag)	#3 charge (0.298 kg/bag)	#4 charge (0.425 kg/bag)	#5 charge (0.709 kg/bag)
155a	0	0	0	8	10
155b	0	0	0	18	18
155c	1	1	1	14	13

3.2.2 Ignition method

The lines were ignited using a railroad fusee (or flare) [13] connected to approximately 4 feet of safety fuse, as shown in Figure 11. The flares used were the same as those used to indicate obstacles or advise caution on roadways at night, and they burn with a bright red light. They are commonly found in roadside emergency kits. The safety fuse gives the explosives expert enough time to walk to a safe distance from the set-up area before the flare and gun propellant ignite. This procedure for igniting excess gun propellant is commonly used in the Canadian Forces. It is described in Department of National Defence literature [1]. The flare is composed of strontium nitrate, sulphur, potassium perchlorate, sawdust and paraffin wax (in unknown proportions) [14].

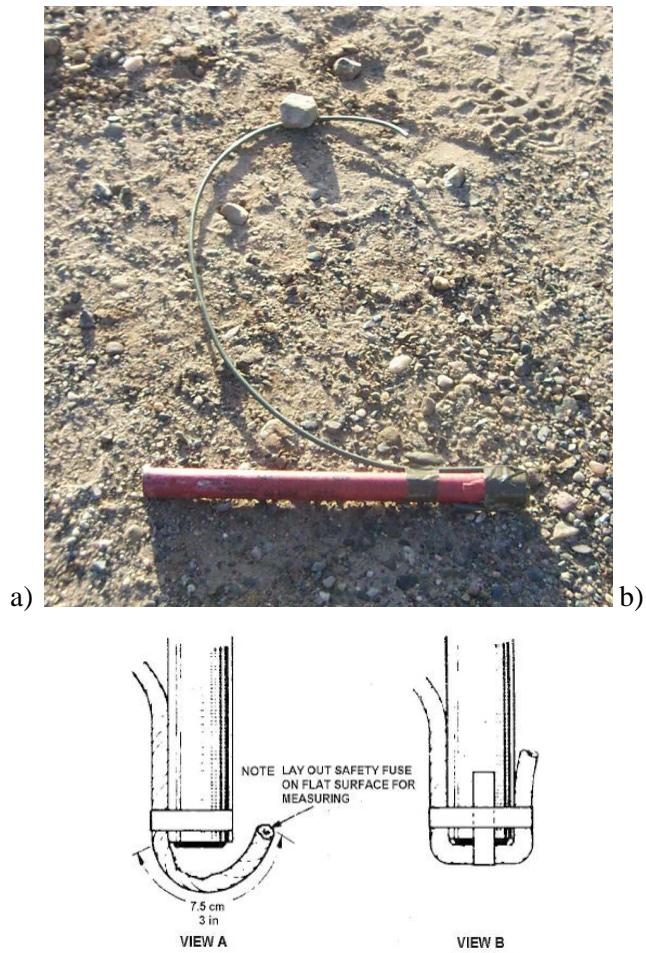


Figure 11: Typical flare, with a safety fuse for igniting the gun propellant: a) photograph of the set-up, b) schematic showing how a railroad fusee is prepared for ignition

The lines of gun propellant were laid parallel to one another on the ground. As only one flare was available for ignition, the lines were connected with propellant, either in bags or as free grains, as shown in Figure 12, to ensure that all the lines ignited. At the time when this trial was conducted, it was not known that the flare was the potential source of dioxins and furans. The flare was inserted underneath the first gun propellant line, and the safety fuse was lit with a match. All personnel went to a secure distance (50 m) from the set-up and waited for ignition. The fire was intense, as shown in Figure 13, but lasted for only 30 seconds or so.

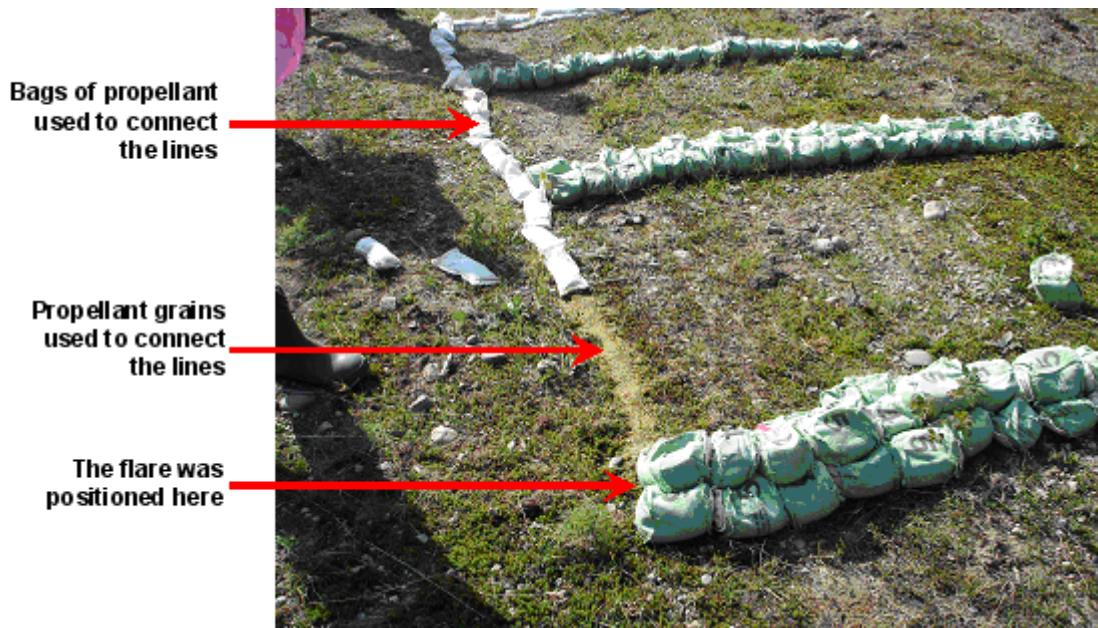


Figure 12: Lines of propellant bags before ignition



Figure 13: Burning the gun propellant lines

3.3 Experiment set-up: the flare trial

Following the results obtained from the burning trial on surface soil described above and discussions with Mr. Michael Walsh from the Cold Regions Research and Engineering Laboratory (CRREL), a second trial was organized to determine if a flare was necessary for the production of dioxins and furans. Two trials were carried out: 1) burning on sand; 2) burning on stainless-steel plates. The test on sand was set up so as to collect samples in three conditions:

- 1) gun propellant burned near the railroad fusee
- 2) gun propellant burned far from the fusee
- 3) the railroad fusee was ignited by itself, without gun propellant.

The test on stainless-steel plates was set up so as to collect samples in two conditions:

- 1) gun propellant burned near the railroad fusee
- 2) gun propellant burned far from the fusee.

3.3.1 Set-up description for burning on sand

This trial was conducted in winter (9 and 10 February 2009). As propellant burns differently on soil and snow [2-4], a layer of clean sand approximately 5 cm thick was poured onto the snow cover, and the propellant and a flare were put on top of it. Three samples were taken during this trial.

A schematic of the set-up is shown in Figure 14. Lines 1 and 2 were composed of four bags each from 105-mm-calibre M67 propelling charges (previously described in section 3.1): two #6 and two #7 charge bags, for a total of 1.332 kg of gun propellant. Line 1 had a railroad fusee for ignition. A line of propellant grains was spread between lines 1 and 2 to connect them and ensure proper ignition of line 2. Photographs of the trials appear in Figures 15 and 16.

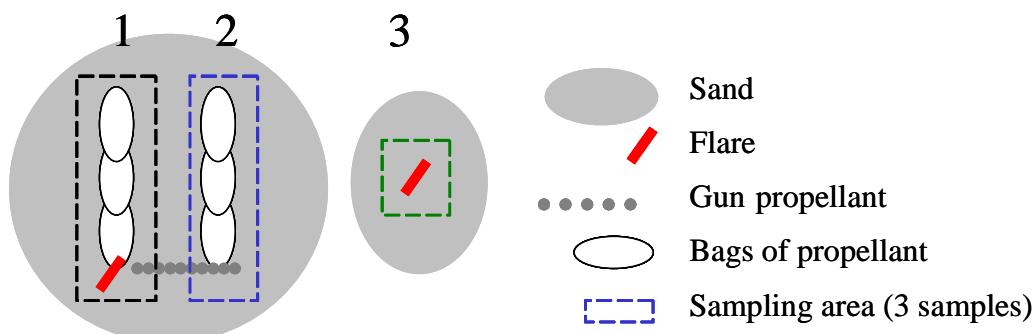


Figure 14: Schematic of the set-up for the flare trial

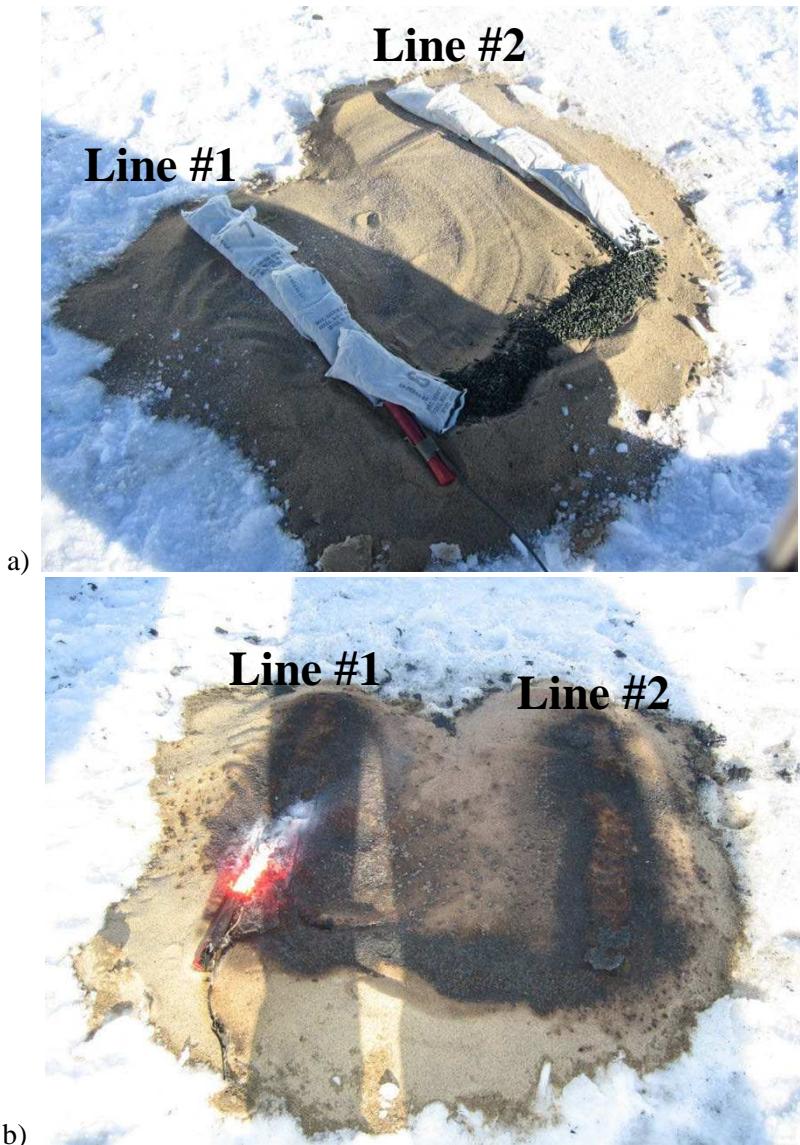


Figure 15: Set-up for the flare trial: a) before and b) after combustion (lines 1 and 2)



Figure 16: Set-up for the flare trial (the part with the flare only: line 3)

3.3.2 Set-up description for burning on stainless-steel plates

To avoid any dilution of the samples by sand sampled with the burn residues, burns were also conducted on stainless-steel plates. The set-up used was developed by Dr. Sonia Thiboutot from DRDC Valcartier [15]. It consisted of a large table made of stainless steel (3 x 1.5 m), shown in Figures 17 and 18, on which excess gun propellant bags were placed and ignited. A railroad fusee, of the type used in the other trials, was used for ignition. The flare was put in a corner, as seen in Figure 18, and propellant was placed on the table. A total of 150 kg of bags (105-mm calibre, unknown numbers of #5 to #7 bags) was used in the two trials, as seen in Figure 19.

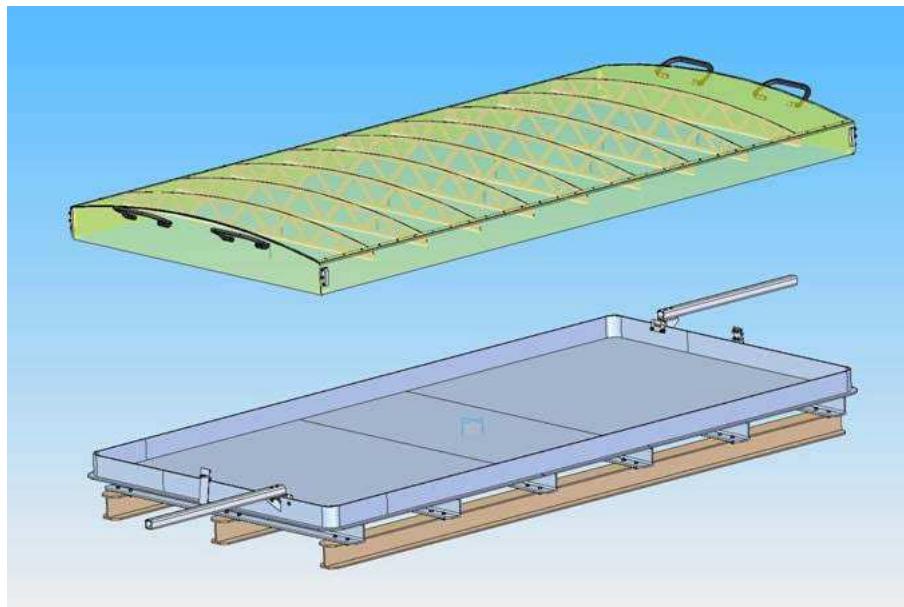


Figure 17: Schematic of the stainless-steel burning table



Figure 18: The flare in one corner of the table



Figure 19: Gun propellant bags on the table before ignition

3.4 Sampling

3.4.1 Sampling in the propellant burning trial on soil

For the initial trial, two soil samples were taken at the burning site before the gun propellant lines were set up, to determine whether there was any dioxin or furan background at the trial location. The area where the background samples were taken and where the set-up was later placed is shown in Figure 20a. Some very short grass and moss was present, but most of the soil was free of vegetation. Two samples were taken, each composed of 25 increments taken over the entire area of the future burn at a maximum depth of 1 cm (0 to 1 cm).

As seen in Figure 20b, the burn marks were obvious after the fire, with black lines of soot. It is known that, as gun propellant burns, intact grains are often “kicked off” from the fire, to be later found intact after the burning [2-4]. No intact gun propellant grains were observed anywhere after this trial. A close-up of a line is shown in Figure 21. Sampling began once the lines cooled down. One surface sample was taken in the combustion path for each line, taking care to sample only soot residue, with as little soil as possible. Another sample was taken under the combustion path, 0 to 1 cm deep. A duplicate was taken for some samples. A small shovel was used (see Figure 21), and it

was cleaned with solvent and paper towels between each sampling to reduce sample cross-contamination (acetone-water-acetone). Samples were put in a 250-mL amber glass jar, which was placed in a cooler with ice after the sampling. Samples were kept at 4°C until their analysis.



Figure 20: Set-up area: a) before the set-up installation (flags indicate the positions of the future gun propellant lines) and b) after the burning.



Figure 21: Close-up of a line after combustion

3.4.2 Sampling for the flare trial: sand and stainless-steel table

In the trial on sand, three samples were collected after burning (see Figure 14) and sent for analysis as described in section 3.5. Care was taken to wash the shovel with acetone after each sample. The samples were composed of the combustion residues (gun propellant and/or flare) and some sand.

In the trial on the stainless-steel table, samples were taken at three different locations on the table after combustion. The first sample was composed of flare residue (white solid), the second sample was composed of black gun propellant residue around the flare, and the third one was taken in the middle of the table, away from the ignition point, as shown by the arrows in Figure 22. No background sample could be taken for burning on the stainless-steel table, because there was no material to sample.



Figure 22: Table after burning and sampling positions

3.5 Analytical method for determining dioxins and furans in solid samples

All the samples were sent to a private company (Biolab, Thetford Mines, Quebec) for analysis. Dioxins and furans were extracted from the solid samples by liquid extraction with toluene in a Soxhlet apparatus. Following purification, the dioxins and furans were concentrated and analysed by means of gaseous-phase chromatography coupled to a high-resolution mass spectrometer (GC-MS). The method was developed by the *Centre d'expertise en analyse environnementale du Québec* (method MA.400 – D.F. 1.0) [16]. For chlorinated dioxins and furans, it is not possible to express a quantification limit in toxic equivalents (TEQs). The detection limit for this method is 0.1 pg/g for each of the congeners measured. The concentrations obtained were then converted into TEQs by means of Equation 1.

4 Results and discussion

4.1 Dioxins and furans in residues after the gun propellant burning trial on soil

The results of the dioxin and furan analyses are shown in Table 9. In the following discussion, samples will be referred to using numbers (BOP-1 to BOP-16), as shown in Table 9. The analyses of the background samples (BOP-1 and -2) demonstrated that the soil chosen for the experiment was not free of dioxins and furans. The contamination may be anthropogenic and/or natural (unknown at this moment). An average of 0.33 pg TEQ/g was detected in the first cm of soil. The amount of soil in the background samples was not the same as the amount in the samples taken in the burning areas. In the burn marks, the sample was composed mostly of combustion residues. Because of this, the TEQ concentration of PCDD/PCDF in the background samples was not subtracted from the concentration in the other samples. The following discussion uses the raw data to compare the lines with one another.

Following the burning of 105-mm-calibre gun propellant on surface soil, the samples taken directly on the soot line (mostly residue, with a small quantity of soil), i.e., samples BOP-3, -4 and -5, showed values of 0.073, 0.06 and 0.1 pg TEQ/g, respectively. These values, being lower than the background level, were not expected. The values for the samples taken from under the combustion path (at a soil depth of 0 to 1 cm, samples BOP-9, -10 and -11) showed values of 0.24, 0.15 and 0.26 pg TEQ/g. These values were closer to the value obtained for the background samples. A possible explanation for this result is that the concentration in the residue was very low and simply diluted the concentration of dioxins and furans in the soil, which was already contaminated from previous trials at this site.

Regarding the lines where 155-mm-calibre propellant bags were burned, the values for the residues in samples BOP-6, -7 and -8 were 0.086, 0.094 and 0.098 pg TEQ/g, respectively. Again, these values were lower than the values for the background samples. The results for the samples taken from under the burnt pads (at a soil depth of 0 to 1 cm, samples BOP-12, -13 and -14) showed values of 0.26, 0.18 and 0.17 pg TEQ/g. The explanation provided previously for the burning of 105-mm bags also applies here.

Table 9: Concentrations of dioxins and furans, reported in toxic equivalent quantities, in the samples of gun propellant burned on soil

Sample No.	Line identification and sampling type*	Toxic equivalent quantity (TEQ) for dioxins and furans (pg/g)
BOP-1	Background (surface)	0.34
BOP-2	Background (0-1 cm deep)	0.33
BOP-3	105a (surface)	0.073
BOP-4	105b (surface)	0.06
BOP-5	105c (surface)	0.1
BOP-6	155a (surface)	0.086
BOP-7	155b (surface)	0.094
BOP-8	155c (surface)	0.098
BOP-9	105a (0-1 cm deep)	0.24
BOP-10	105b (0-1 cm deep)	0.15
BOP-11	105c (0-1 cm deep)	0.26
BOP-12	155a (0-1 cm deep)	0.26
BOP-13	155b (0-1 cm deep)	0.18
BOP-14	155c (0-1 cm deep)	0.17
BOP-15	105a (surface) duplicate	0.11
BOP-16	155a (surface) duplicate	0.33

* Surface = sample taken directly in the combustion path, residue collected with as little soil as possible

0-1 cm deep = sample taken under the combustion path (soil depth of 0 to 1 cm)

It seems that the combustion of gun propellant does not produce dioxins or furans as expected. As discussed in section 2.2, a preliminary analysis was performed on samples taken from burns of gun propellant on snow, and dioxins and furans were detected at values exceeding the regulations in three of the five samples analysed. One logical explanation is that the production of dioxins and furans is possible only when a flare is present with the organic material to be burned (i.e., gun propellant in this case). One of the main ingredients in the flare is potassium perchlorate, which is believed to react with gun propellant at high temperatures to form dioxins and furans. This is consistent with the EPA statement in Reference [17], according to which the formation of dioxins and furans requires the presence of a chlorine donor (a molecule that provides a chlorine atom to the

pre-dioxin molecule) and the formation and chlorination of a chemical intermediate that is a precursor. During the experiment performed on snow (section 2.2 of this report and Reference [4]), one flare was used for every trial (i.e., one flare for each propellant line, with no lines connected by grains to assure flame propagation), and most of the residue plume was collected and combined into one large sample. In the propellant combustion trial on surface soil discussed in this report, only one flare was used to ignite all six lines, and care was taken during sampling not to sample in the flare residue, because the flare was not then suspected of being the source of dioxins and furans. That would explain the low TEQ levels measured.

Because the dioxins and furans seem to have been created when the flare was present, it would have been normal to detect these compounds in most of the samples that were produced in Diaz's trial (burning of propellant on snow [4] and section 2.2 of this report). As discussed previously, no dioxins or furans were detected in samples 1 and 2 (see Table 2), and this remains unexplained at this time. The reason may be that the amount of residue was much larger than in the other samples (see Table 2), so dilution was too great to allow detection. Following this hypothesis, in the combustion trial on surface soil, after the six lines of gun propellant were burned on the soil, only one line could have presented some dioxins and furans (line 155c, because the flare was placed at its end), but the value detected was still below the background value. This can be explained by the fact that the residue was not sampled all at once, but in increments, and by the fact that sampling was avoided near the flare. As stated earlier, when this first trial was organized, the flare was not suspected of being necessary to produce dioxins and furans during burning. The flare trial described in section 3.3 was thus organized. In this trial, samples closer to the position of the flare were collected for analysis. The results are discussed in the next section.

4.2 Dioxins and furans in residues after the flare trial: sand and stainless-steel table

The results of the flare trial are shown in Table 10 for the trial on sand, and in Table 11 for the trial on the stainless-steel table. In the case of the trial on sand, the toxic equivalent quantities (TEQs) measured in the samples were very low (0.00006 to 0.04 pg/g), and it is hard to draw a conclusion from them.

On the other hand, the trial performed on the stainless-steel table produced more conclusive results (Table 11). Sampling directly on steel avoids any dilution of the residues. The result was that the concentrations of dioxins and furans (reported as TEQs) were higher in the area near the flare (5.182 pg/g) than in an area that was not in contact with the flare (the middle of the table, 0.068 pg/g). The residues from the flare itself showed an intermediate value (0.337 pg/g). The presence of the flare seems to be

responsible for the production of dioxins and furans. Since this trial was not replicated, these values should be taken only as an indication that flares produce dioxins and furans when burned with gun propellant and should not be used for any further calculation. The values obtained in the residue are much lower than those seen in the burns on snow cover (see section 2.2). As previously indicated, dioxins and furans were detected in three out of five samples (29.5, 31.8 and 10.9 pg/g) (Table 2). These values were obtained from a large sample, while the values obtained from the samples of burnt propellant on the steel table were obtained from a much smaller sample. The quantity of dioxins and furans produced with a single flare was clearly higher during burning on snow. This can be explained by the fact that these molecules are produced during incomplete combustion, as when gun propellant is burned on snow [2-4]. It is believed that combustion is slowed by the presence of melted snow and that the perchlorate in the flare reacts with the carbon-based molecules in the propellant to form precursors of dioxins and furans and then dioxins and furans themselves. These molecules are probably not further decomposed into other molecules, such as gases, and are retained in the residue, probably due to the lower temperature in the combustion zone.

In the case of the flare trial on sand (results in Table 10), it is believed that the very small quantities measured were due to dilution by sand sampled with the residues. In the trial presented in Chapter 3 (gun propellant burning on surface soil), the sampling was also performed on soil, but since the soil was more compact (natural soil versus loose sand in the flare trial), a higher proportion of residue was probably analysed. Overall, the results of the flare trial on sand are considered non-conclusive, and the use of the stainless-steel table for burning was thought to be the best approach for sample collection.

The toxic equivalent quantity of the dioxins and furans in the flare residues in the trial on sand was lower than in the trial on the stainless-steel table. This can be explained by the fact that sand was present in one set of samples (from the trial on sand), but not in the other. This caused a dilution of the concentration.

Table 10: Concentration of dioxins and furans, reported in toxic equivalent quantities, in the samples from the flare trial on sand

Sample No.	Description	Toxic equivalent quantity (TEQ) of dioxins and furans (pg/g)
1	Propellant + flare residues + sand	0.00006
2	Propellant residues + sand	0.00009
3	Flare residues + sand	0.04006

Table 11: Concentrations of dioxins and furans, reported in toxic equivalent quantities, in the samples from the flare trial on the stainless-steel table

Sample No.	Description	Toxic equivalent quantity (TEQ) of dioxins and furans (pg/g)
1	Flare residue	0.337
2	Propellant residues near flare	5.182
3	Middle of table (propellant residues only)	0.068

5 Alternate methods that reduce the production of dioxins and furans

The results presented in this report show that the burning of excess gun propellant produces dioxins and furans probably because of the presence of a railroad fusee as the ignition source. This production is worse when the burning is performed on snow cover, owing to more incomplete combustion. Burning performed on a stainless-steel table demonstrated that, even if the burning is more complete, dioxins and furans are still produced, again due to the presence of the igniter. The procedure for burning excess gun propellant bags should be modified to reduce or avoid the production of dioxins and furans.

One way to achieve this goal would be to remove the chlorine source, i.e., the railroad fusee containing perchlorate. Ignition could be achieved using a chlorine-free device with delayed activation, to give enough time for soldiers to withdraw from the burning site to a safe distance. The procedural manual for *Destruction of duds and misfired ammunition on CF ranges and training areas* [1] should be modified to reflect the findings in this report. Other procedures for initiating combustion should be investigated.

It must also be noted that the burning of excess gun propellant produces other residues considered hazardous to the environment, because they contain energetic materials [2-4], such as 2,4-DNT, and heavy metals, such as the lead present in the #5 bag of the M67 propelling charge for the 105-mm howitzer [11]. The whole concept of open burning on the ground should be revised to avoid the contamination of surrounding soils. Moreover, it is believed that the burning of excess gun propellant on snow cover should be completely avoided, because combustion is incomplete due to the presence of melted snow, and this results in the production of a greater quantity of pollutants, such as 2,4-DNT. Acceptable alternative methods, such as using modular charges or recycling excess gun propellant, were proposed by Diaz *et al.* [4] and should be considered. More research and development is needed for these two options, but both would avoid the burning of excess propellant and also avoid the use of flares for ignition. If the burning of excess propellant bags is unavoidable, the associated environmental risks could be lessened by burning the bags in an incinerator equipped with a gas treatment system to reduce the toxic emissions. The future construction of a demilitarization capability at CFB Dundurn [18] could offer a very interesting solution, but this will not be available for a few years, so a short-term solution must be considered. One of these short-term solutions is to develop a portable stainless-steel table to conduct the burns. Such a table is currently being studied by Dr. Sonia Thiboutot from DRDC Valcartier [15]. This would avoid any contact between the soil and the residues and prevent any leaching into the soil and groundwater. For these last options, ignition should not be performed with a flare, to avoid the production of dioxins and furans, and the residues produced should be treated as hazardous materials in accordance with environmental regulations.

6 Conclusion

Excess gun propellant remaining after artillery exercises is burned at many ranges and training areas across Canada. The work presented in this report demonstrates that the destruction of excess propellant by open burning on the ground using a railroad fusee (flare) for ignition produces polychlorodibenz-p-dioxins (PCDD, dioxins) and polychlorodibenzofuranes (PCDF, furans). These compounds are known to be toxic and persistent in the environment. The use of a flare containing perchlorate for ignition was identified as the cause of the formation of dioxins and furans. Moreover, the burning of propellants on snow cover produces more contaminants than burning on ground. We recommend that the burning tests (both on snow and on a stainless-steel table) be replicated to confirm these conclusions with further sets of data. The burning procedures should then be revised to reflect the results presented in this report and the findings of the future trial.

Replacing the flare with some other device that contains no perchlorate will prevent the formation of dioxins and furans. One short-term solution that we propose is to perform future burns of excess gun propellant without a flare and on stainless-steel tables (ongoing work by Dr. Sonia Thiboutot from DRDC Valcartier [15]. This would also prevent the combustion residues from coming into contact with the soil and leaching into the environment. The development of a demilitarization system, including an incinerator equipped for gas treatment, is also considered a solution. Further testing with the stainless-steel table will include measuring the dioxins and furans produced by various ignition methods to confirm the results obtained in the present study. An alternate ignition method free of perchlorates is sought.

It is not believed that using flares by themselves, to warn of danger on roads, for example, produces major quantities of dioxins and furans, if there is a limited amount of organic material in the combustion zone. Neither the thin paper wrapping around the flare nor the presence of paraffin and sawdust in the composition should produce significant quantities of dioxins or furans. In addition, combustion should be almost complete, because the flare is held upright by metal wires.

Finally, to completely avoid the burning of excess gun propellant, developing modular 105-mm charges or recycling propellant would provide a solution, since there would be no excess bags to destroy by burning.

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Annex A Toxic equivalency factors

Table 12: Toxicity equivalency factors (TEFs) for polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs), as proposed by the World Health Organization (WHO) [19]

Compounds	TEF
<i>Chlorinated dibenzo-p-dioxins (CDD)</i>	
2,3,7,8-tetra CDD	1
1,2,3,7,8-penta CDD	0.5
1,2,3,4,7,8-hexa CDD	0.1
1,2,3,6,7,8-hexa CDD	0.1
1,2,3,7,8,9-hexa CDD	0.1
1,2,3,4,6,7,8-hepta CDD	0.01
Octa CDD	0.001
<i>Chlorinated dibenzofurans (CDF)</i>	
2,3,7,8-tetra CDF	0.1
1,2,3,7,8-penta CDF	0.05
2,3,4,7,8-penta CDF	0.5
1,2,3,4,7,8-hexa CDF	0.1
1,2,3,6,7,8-hexa CDF	0.1
2,3,4,6,7,8-hexa CDF	0.1
1,2,3,7,8,9-hexa CDF	0.1
1,2,3,4,6,7,8-hepta CDF	0.01
1,2,3,4,7,8,9-hepta CDF	0.01
Octa CDF	0.001

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List of symbols/abbreviations/acronyms/initialisms

BFC	Base des Forces canadiennes
CCME	Canadian Council of Ministers of the Environment
CFB	Canadian Forces Base
cm	Centimetre
CBI	Clean-burning igniter
CRREL	Cold Regions Research and Engineering Laboratory
DRDC	Defence Research & Development Canada
°C	Degree Celsius
DND	Department of National Defence
2,4-DNT	2,4-dinitrotoluene
DRDKIM	Director Research and Development Knowledge and Information Management
EPA	Environmental Protection Agency
GC-MS	Gaseous-phase chromatography coupled to mass spectrometry
GPS	Global positioning system
g	Gram
kg	Kilogram
L	Litre
m	Metre
mL	Millilitre
mm	Millimetre
METC	Munitions Experimental Test Centre
nd	Not detected
%	Percentage
pg	Picogram
PCDF	polychlorodibenzofuranes
PCDD	Polychlorodibenzo-p-dioxins
R&D	Research and development

SERDP	US Strategic Environmental Research and Development Programme
TEF	Toxic equivalency factor
TEQ	Toxic equivalent quantity

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<p>4. AUTHORS (last name, followed by initials – ranks, titles, etc. not to be used)</p> <p align="center">Poulin, I.; Thiboutot, S.; Brochu, S.</p>		
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The burning of bags of excess gun propellant left over after an artillery exercise is a common practice on Canadian Forces Base (CFB) ranges and training areas. This process is carried out by aligning and burning the bags on the ground. This operation is known to leave significant quantities of energetic residues. It was also suspected of producing, among its combustion products, dioxins and furans, two structurally and chemically related chlorinated compounds known to be toxic and persistent in the environment. At CFB Petawawa, dioxins and furans were detected in some soil and water samples. The work reported here was aimed at studying the potential production of dioxins and furans from the combustion of gun propellants using a flare as an igniter. The results indicated that this production was not related to the combustion pattern, chemical composition or mass of the gun propellant, but to the presence of the igniter. The accepted procedure published by the Canadian Forces requires the use of a railroad fusee or a flare (like the warning flares used on roads at night) as the ignition source for the gun propellant. This trial should be replicated, and if further trials confirm that the railroad fusee is the source of the dioxins and furans, the disposal procedure for excess gun propellant by open burning should be modified.

Le brûlage de gargousses excédentaires de poudre propulsive non utilisées après un exercice de tir de l'artillerie est pratique courante sur les champs de tir et d'entraînement des bases des Forces canadiennes (BFC). Ce procédé est effectué en alignant et en brûlant au sol les gargousses de poudre. Il est reconnu que cette opération laisse une quantité significative de résidus de matériaux énergétiques. Parmi les produits de combustion, cette procédure pourrait également produire des dioxines et des furannes, deux familles de produits chlorés structurellement et chimiquement semblables reconnus comme étant toxiques et persistants dans l'environnement. À la BFC Petawawa, des dioxines et des furannes ont été détectés dans certains échantillons de sols et d'eaux souterraines. Le travail présenté dans ce rapport visait à étudier la relation entre le brûlage de poudres propulsives et la production de dioxines et de furannes. Les résultats semblent indiquer que la production de ces composés n'est pas liée au modèle de combustion, à la composition chimique ni à la masse de poudre utilisée, mais à la présence de l'allumeur. La procédure prônée par les Forces canadiennes et publiée dans les documents internes exige l'utilisation d'une fusée éclairante (similaire à celles utilisées sur les routes pour la signalisation de nuit) pour l'allumage de la poudre. D'autres réplicats des tests devront être effectués et s'il est confirmé que la fusée est la source de la production de dioxines et de furannes, la procédure actuelle de disposition des gargousses non utilisées par brûlage devrait être modifiée.

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Gun propellant; artillery; open burning; combustion; environmental characterization; residues; dioxins; furans; military training; ranges and training area; sustainability, energetics.

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